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A new pyrolysis-based thermochemical conversion option to produce value-added chemicals from lignocellulosic biomass

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ABSTRACT

Pyrolysis of lignocellulosic biomass leads to an array of useful solid, liquid and gaseous products. Staged degasification is a pyrolysis-based conversion route to generate value-added chemicals from biomass. Because of different thermal stabilities of the main biomass constituents hemicellulose, cellulose and lignin, different temperatures may be applied for a step-wise degradation into valuable chemicals. Staged degasification experiments were conducted with deciduous (beech, poplar), coniferous (spruce) and herbaceous (straw) biomass. Thermogravimetry was used to estimate appropriate temperatures for a two-stage degradation process that was subsequently evaluated on bench-scale by moving bed and bubbling fluidised bed pyrolysis experiments. Degasification in two consecutive stages at 250–300 °C and 350–400 °C leads to mixtures of degradation products that originate from the whole biomass. The mixtures that were generated at 250–300 °C, predominantly contain hemicellulose degradation products, while the composition of the mixtures that were obtained at 350–400 °C, is more representative for cellulose. Lignin-derived fragments are found in both mixtures. Yields up to 5 wt% of the dry feedstock are obtained for chemicals like acetic acid, furfural, acetol and levoglucosan. Certain groups of thermal degradation products like C_2–C_4 oxygenates and phenols are formed in yields up to 3 wt%. Highest yields have been obtained for beech wood. Staged degasification is a promising pyrolysis-based route to valorise lignocellulosic biomass. Clear opportunities exist to increase product yields and selectivities by optimisation of reactor conditions, application of catalysts and specific biomass pretreatments like demineralisation and pre-hydrolysis.

1. Introduction

Pyrolysis can be defined as the direct thermal decomposition of matter in the absence of oxygen. When applied to biomass, an array of useful products can be produced, liquid and solid derivatives and fuel gases. Already in the 1950s more than 200 chemical compounds had been identified from the pyrolysis of wood [1]. Before the onset of the petrochemical era in the beginning of the 20th century, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks [2–4]. Recently, the global problems that are associated with the intensive use of fossil fuels (global warming, depletion of natural resources, security of supply of energy and materials) have led to a renewed interest in (modern varieties of) these processes. The fact that different biomass constituents react differently at different temperatures to yield different spectra of products [5–8] can be exploited to extract value-added chemicals from biomass as a renewable route to products that can be regarded as petrochemical substitution options [9,10]. The concept of staged degasification is a low-temperature thermochemical conversion route to generate value-added chemicals from lignocellulosic biomass. Fig. 1 presents a schematic overview of the staged degasification concept and its place in a thermochemical biorefinery.

The main biomass constituents hemicellulose, cellulose and lignin can be selectively devolatilised into value-added chemicals. This thermal breakdown is guided by the order of thermochemical stability of the biomass constituents that ranges from hemicellulose (fast degassing/decomposition from 200 to 300 °C) as the least stable polymer to the more stable cellulose (fast degassing/decomposition from 300 to 400 °C). Lignin exhibits an intermediate thermal degradation behaviour (gradual degassing/

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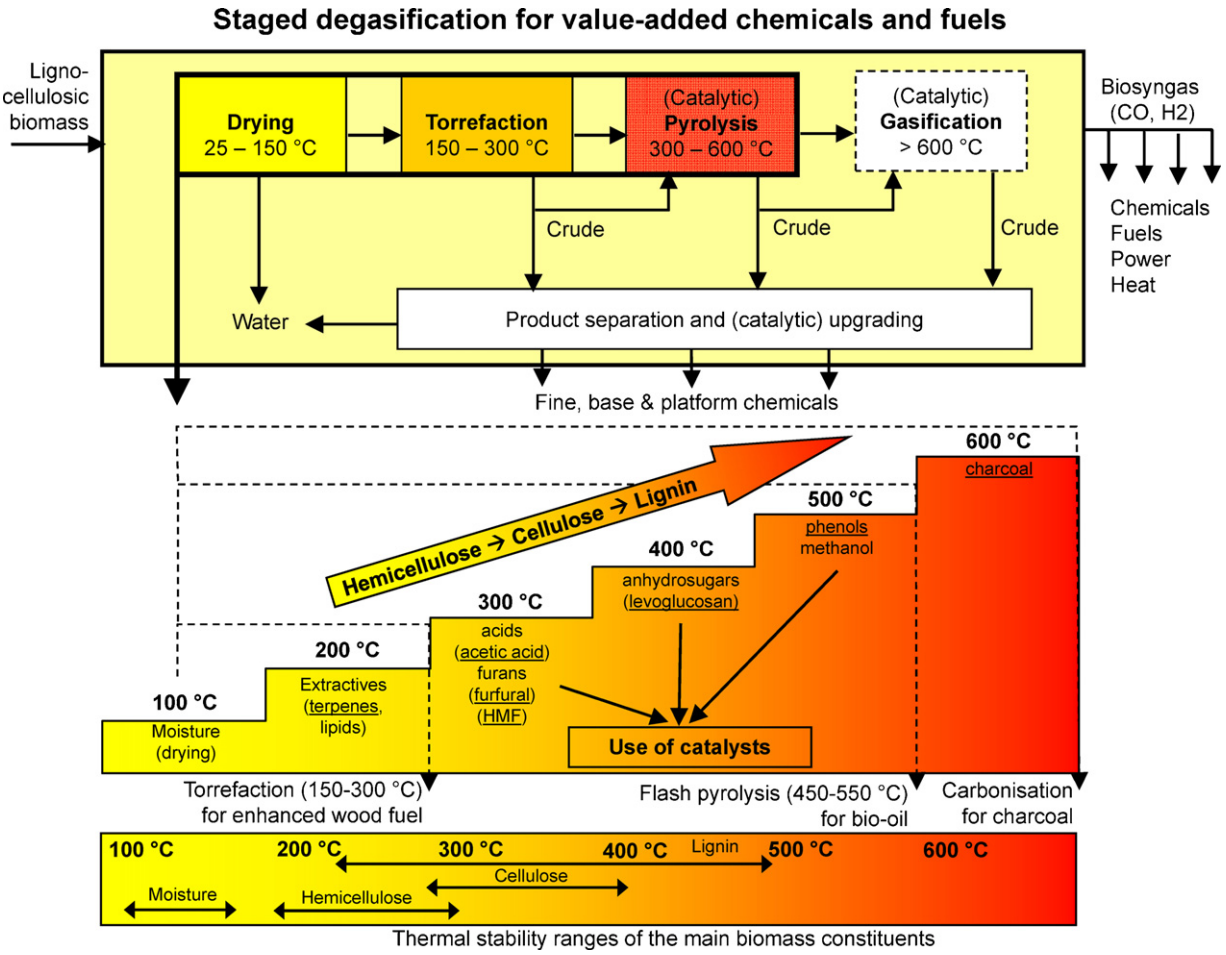

Fig. 1. Staged degasification concept within the thermochemical biorefinery.

decomposition from 250 to 500 °C). Results obtained for beechwood in principle acknowledge the view that the chemical wood components are decomposed in the order of hemicellulose–cellulose–ligin, with a restricted decomposition of the ligin at relatively low temperatures. In the further course of heating, a recondensation of the lignin takes place, whereby thermally largely stable macromolecules develop [11–13]. Whereas both hemicellulose and cellulose exhibit a relatively high devolatilisation rate over a relatively narrow temperature range, thermal degradation of lignin is a slow-rate process that commences at a lower temperature when compared to cellulose.

Since the thermal stabilities of the main biomass constituents partially overlap [14] and the thermal treatment is not specific, a careful selection of temperatures, heating rates and gas and solid residence times is required to make a discrete degasification possible when applying a step-wise increase in temperature. To enhance the selectivity towards wanted products, catalysts can be applied as impregnants of the biomass, or as an external aid, e.g. in the form of the fluidisation material in a fluidised bed reactor or in the form of a catalytically active fluidisation gas (steam, hydrogen, oxygen, CO_2). Downstream treatment of the primary product vapours in a fixed bed of catalyst is another possibility. Depending on these process conditions and parameters like biomass composition, and the presence of catalytically active materials, the product mixture is expected to contain more or less degradation fragments from hemicellulose, cellulose or lignin. The staged degasification approach stands in contrast with fast pyrolysis technology [15,16], in which the biomass is rapidly heated up to temperatures around 500 °C, causing an almost instantaneous release of a myriad of thermal degradation products that are quickly quenched to a so-called 'pyrolysis-oil'. It is obvious that the extraction of value-added chemicals from this complex mixture of thermal degradation products is a challenge. In their critical review on pyrolysis-oil, Mohan et al. [17] present an extensive overview of pyrolysis-oil and related issues. Whereas fast pyrolysis of biomass primarily has been developed to maximise liquid product yield, staged degasification aimes at the gentle devolatilisation of thermal degradation products from the biomass. Hereby it is assumed that type, yield and selectivity of the liberated products can be influenced by matching the process conditions of the degasification process with the thermal stability of the main biomass constituents. Due to the relatively mild conditions, the overall product spectrum might be less complex, more stable and less prone to unwanted secondary reactions when compared to the harsher fast pyrolysis process where all three biomass components are degraded simultaneously and at the same temperature. Recently, a limited number of value-added chemicals from biomass has been identified in an extensive study by NREL/PNNL [18,19]. For the carbohydrate fraction of the biomass (hemicellulose and cellulose) furfural [20] and levoglucosan [21] are interesting value-added chemicals that can possibly be produced by direct thermochemical conversion.

Although several ('dry') thermochemical processes for furfural production have been explored in the last decades [22,23], modern commercial processes to produce furfural involve mostly aqueous-phase hydrolysis/dehydration processes operating at relatively

low temperatures (around 200 °C) and often using catalysts like sulphuric acid. This leaves the anhydrosugar levoglucosan (dehydrated glucose) as the most interesting candidate that could be directly produced from the carbohydrate fraction of biomass by (staged) degasification or pyrolysis. Alternatively, staged degasification could be targeted at the production of groups of chemicals that can be upgraded using existing (petro)chemical technology like selective hydrogenation [24]. Examples of these groups are carboxylic acids (formic, acetic, propionic), furans (furfural, furfuryl alcohol, furanone, hydroxymethylfurfural), C_2, C_3 and C_4 oxygenates (hydroxyacetaldehyde, glyoxal, acetol), anhydrosugars (predominantly levoglucosan) and hydroxylated aromatics and aromatic aldehydes which constitute potential thermochemical degradation products from lignin. It is obvious that the separation and subsequent upgrading of these groups of chemicals is easier and cheaper than the isolation of a single chemical from the complex mixture of thermal degradation products. Whether the staged degasification approach holds a promise to selectively produce value-added chemicals from lignocellulosic biomass in good yields, is the focus of the experimental 'Proof of Principle' study that is described in this paper.

2. Materials and methods

Beech and poplar have been chosen as representative for deciduous woods (hardwoods), spruce as an example of a typical coniferous wood (softwood) and wheat straw as a representative for a herbaceous type of biomass (grass, agricultural residue). The beech wood is commercially available from Rettenmaier, Germany (Räuchergold, particles of 0.75–2 mm and 2–16 mm). The poplar wood was kindly provided as 4 cm × 4 cm chips from freshly debarked and chipped trunks by the Dutch pulp- and paper mill of Mayr-Melnhof in Eerbeek, the Netherlands. The spruce wood was purchased as dry (moisture content approx. 4 wt%) sawdust 0.5–2 mm from Bemap Houtmeel in Bemmel, the Netherlands. Finally, the wheat straw has been obtained in bales as raw undried material from a local farmer in the province of Noord-Holland in the Netherlands.

All feedstocks have been chemically characterised by proximate analysis, (moisture, volatile fraction, ash and fixed carbon), ultimate analysis (C, H, N, O, S and HHV) and elemental analysis (chlorine, metals), using standard chemical analysis methods. For beech, poplar and spruce, indicative values for the content of hemicellulose, cellulose and lignin have been taken from the literature [25]. For straw, analysis results of a representative winter wheat straw have been kindly provided by Wageningen University Research [26].

The thermal behaviour of the chosen feedstocks under pyrolysis conditions was investigated by thermogravimetric analyses (TGA) and differential thermogravimetric analysis (DTG) with a Mettler Toledo TGA 850, featuring automated temperature and weight control and data acquisition. Samples were milled and sieved to an approximate particle size of 0.1 mm. Prior to the analysis, samples were dried overnight in a stove at 105 °C under air. The sample weight amounted to approx. 15 mg. Samples were heated at 10 °C/min for the drying step (30 min at 100 °C). Subsequently the temperature was linearly increased with 5 °C/min up to the final temperature of 500 °C at which temperature the sample was held for 1 h. Finally the sample was cooled down to room temperature at 50 °C/min. During the whole TGA programme, the sample was kept under a nitrogen flow rate of 45 ml_n/min. Results were interpreted using the procedure, described by Grønli et al. [27].

Pyrolysis experiments were conducted in an auger (screw) reactor and in an bubbling fluidised bed reactor. The auger reactor is a 25 kW_{th} electrically heated, tubular reactor in which the biomass is transported down the length of the reactor tube at a fixed speed by means of a screw at 1–10 kg/h. The installation is equipped with instrumentation for measurement and registration of the gas composition (H_2, CO, CO_2, CH_4, C_xH_y, tar and dust). The reactor is operated continuously and features several axial pyrolysis vapour sampling points and a manually operated char tap at the far end of the reactor tube. Operation and data acquisition is fully automated. Fig. 2 presents a schematic drawing and photograph.

Table 1 contains the main parameters of an experimental programme for two-staged degasification tests in the auger reactor. Degasification temperatures are estimated from the TGA results that indicate the temperature ranges in which the hemicellulose and the cellulose degrade under slow pyrolysis conditions.

Prior to the tests, feedstocks were dried at 105 °C in a stove under air for 12 h. Biomass feeding and collection of char commenced after the reactor was brought to the desired temperature.

Upon reaching stable temperature and gas concentrations, sampling of the pyrolysis vapours was started from the last sampling point at the far end of the reactor at the location of the char collecting pot (Fig. 2).

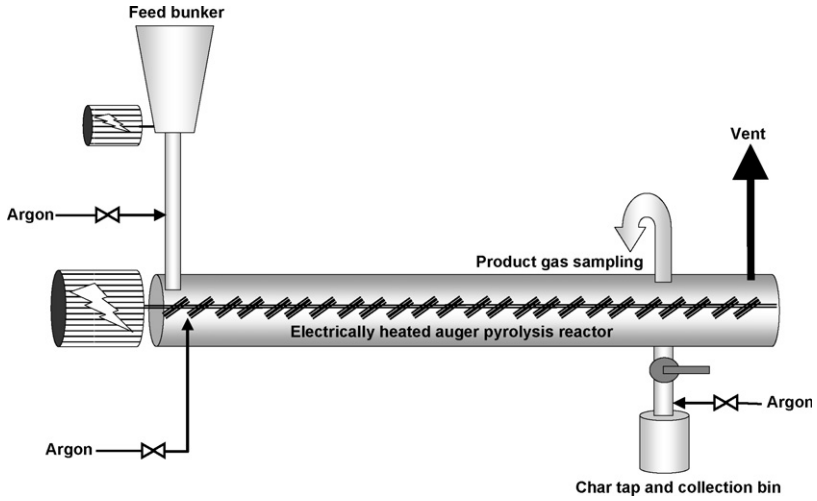

Fig. 2. Schematic and photograph of the auger reactor.

Table 1
Experimental conditions staged degasification tests in the auger reactor

Feedstock	Beech			Poplar		Spruce		Wheat straw	
Shape	Chips			Chips		Sawdust		Milled fibres	
Size	2–16 mm			10 mm		0.5–2 mm		2–20 mm	
Stage	Direct	1	2	1	2	1	2	1	2
Temperature (°C)	350	280	350	280	335	290	345	260	310
Feedstock feed rate (kg/h)	3.6	3.6	2.7	2.3	2.6	1.3	1.3	1.0	1.9
Solids residence time (min)	32	32	32	30	30	30	30	30	30
Reactor fill (%)	30	30	ND	30	34	13	ND	21	35
Ar sweep gas flow rate (Nl/min)	20	20	20	20	20	10	10	10	10
Superficial gas residence time* (min)	0.5	0.6	0.7	0.6	0.5	1.2	1.1	1.2	1.1

* Based on the volume of the empty reactor tube including the screw.

Part of the product gas was sampled using a CEN-certified protocol for sampling of biomass gasification tars [28] and the permanent gases CO, CO_2, CH_4 were monitored on-line by near-dispersive infra-red (ND-IR). Ar was measured on-line with a micro gas chromatograph, equipped with a thermal conductivity detector. The collected pyrolysis vapours are representative for the devolatilisation of the feed during the residence time and may consist of a mixture of devolatilised products and their reaction products from secondary reactions. To prevent these unwanted secondary reactions, Argon was used throughout the experiments as a sweep gas to remove the liberated volatiles from the pyrolysing biomass as fast as practically possible. The collected char from the first stage of a test served as feedstock for the second stage.

Product gas samples were analysed off-line with standard gas chromatography–flame ionisation and mass spectrometric detection (GC/FID/MS) for most organic species, ion-chromatography (IC) for formic acid and Karl-Fisher for water. This standardised method has been developed for the following set of species that are representative for typical thermal degradation products from lignocellulosic biomass: methanol, carboxylic acids (acetic acid, formic acid), other C_2–C_4 oxygenates (acetaldehyde, methylformate, methylacetate, ethylacetate, propanal, acetone, 2-butenal, hydroxy-acetone (acetol), 1-hydroxy-2-butanone), furans (alpha-angelica lactone, 5-methyl-2(3H)-furanone, furfural, 5-methyl-2-furaldehyde, furfuryl alcohol, 2(5H)-furanone, hydroxymethylfurfural), levoglucosan, phenols (2-methoxyphenol (guaiacol), 4-methylguaiacol, phenol, eugenol, 3-ethylphenol, 2,6-dimethoxyphenol, *iso*-eugenol, pyrocatechol, syringaldehyde, hydroquinone), other aromatics (3,4,5-trimethoxytoluene, 1,2,4-trimethoxybenzene). Typically, 40–60% of the total gas chromatographic peak area is attributed to unidentified components. The weight of these unknown components is estimated by a semi-quantitative calibration using the GC-data of the internal standards with the nearest retention time on the GC column.

Compared to the pyrolysis in the auger reactor as a slowly moving bed with external heating only, a bubbling fluidised bed (BFB) of hot sand offers much better heat and mass transfer characteristics. To investigate the effect of this different reactor technology on the staged degasification of lignocellulosic biomass, pyrolysis experiments have been conducted in a 5 kW_{th} atmospheric pressure, 1 kg/h bubbling fluidised bed test facility (Fig. 3) featuring a fully automated operation and data acquisition (pressure, temperature, permanent gases). Beech wood chips (0.75–2 mm) were used as feedstock. To ensure a uniform residence time of the wood particles in the fluidised bed, a fixed amount of 100 g of wood was fed at once. Table 2 presents the main characteristics of the staged degasification experiments in the BFB.

Batch feeding took place with a screw-feeder. In the experiment a single batch of 108 g of the wood particles was fed as quickly as possible into the pre-heated bed (200 °C for stage 1). A mixture of pre-heated (at 300 °C) 20 Nl/min Ar + 0.5 Nl/min N_2 was used as fluidisation gas.

The first stage at 200 °C served as a thermal pretreatment for accelerated drying and for lowering of the degree of polymerisation of the cellulose to facilitate easier depolymerisation during the last degasification stage at 350 °C [29]. In between the subsequent stages, the reactor bed was quickly cooled down to approx. 200 °C to 'quench' the thermal degradation whereafter the temperature was (slowly) raised to the temperature of the next stage. Product gas sampling took place downstream of the cyclone using the procedure described above. Sampling was started prior to feeding and continued well after the moment that the permanent gases that originated from the decomposing beech wood, ceased to

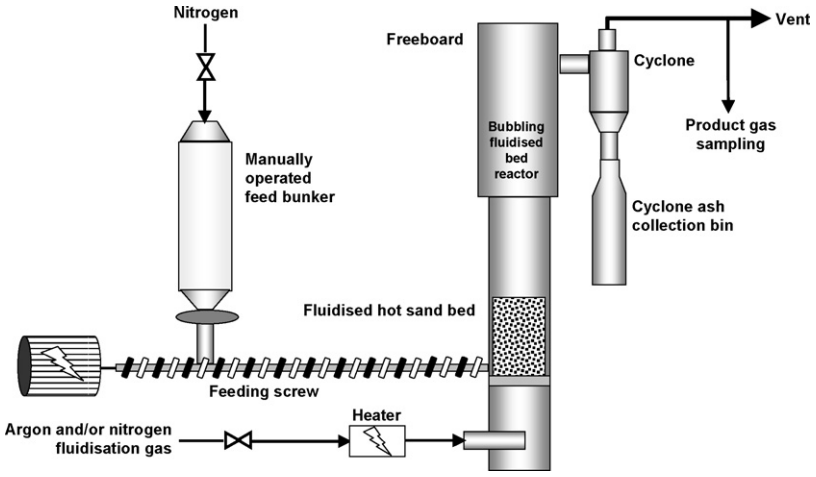

Fig. 3. Schematic of the bubbling fluidised bed test rig.

Table 2
Experimental conditions staged degasification in a bubbling fluidised bed reactor

Stage and temperature (°C)	1, 200	2, 280	3, 350
Estd. heating rate (°C/min)	–	4 (200–>280 °C)	2 (280–>350 °C)
Feedstock	Beech, as received	Char from stage 1	Char from stage 2
Shape and size (mm)	Chips 0.75–2 mm	ND	ND
Amount (g)	108	ND	ND
Feeding procedure	Screw	None, char stayed in bed	Char stayed in bed
Feeding time (s)	6–30	–	–
Solid residence time (min)	60	60	30
Target constituent	Moisture (drying)	Hemicellulose	Cellulose
Bed material	Silica sand	Silica sand	Silica sand
Amount (g)	1000	1000	1000
Shape and size (mm)	Spherical, 0.25 mm	Spherical, 0.25 mm	Spherical, 0.25 mm
Fluidisation gas, flow rate (Nl/min)	Ar, 20 + N_2, 0.5	Ar, 20 + N_2, 0.5	Ar, 20 + N_2, 0.5
Superficial gas residence time* (s)	14	12	10

* Free reactor volume (reactor + cyclone + hot gas particle filter) approx. 8 l.

evolve. It is assumed that the main production of reaction water and organic condensables takes place in parallel with the liberation of CO, CO_2 and CH_4. After the experiment, the reactor was cooled down after which the bed material, consisting of sand and char could be removed and weighed. Attrited bed material and char that had been trapped in the soxhlet filter upstream of the sampling equipment and in the char vessel downstream of the cyclone was collected and weighed as well. Product gas samples were analysed

Table 3
Chemical analysis results feedstocks

Parameter	Unit	Beech[a]	Poplar[b]	Spruce[c]	Wheat straw[d]
Hemicellulose	%, d.b.	30.2	25.6	31.1	23
Cellulose	%, d.b.	44.5	49.0	40.4	34
Lignin	%, d.b.	22.2	23.1	28.2	20
Ash (550)	%, d.b.	0.72	1.05	0.17	7.46
Ash (815)	%, d.b.	0.48	0.83	ND	7.15
H_2O	%, a.r.	Approx. 10	Approx. 54	Approx. 7	Approx. 8
Volatiles	%, d.b.	83.84	83.99	84.76	77.52
Fixed carbon	%, d.b.	15.44	14.96	15.08	15.02
Br	mg/kg, d.b.	<10	<10	ND	<10
Cl	mg/kg, d.b.	19	25	36	204
F	mg/kg, d.b.	<10	<10	6	<10
HHV	J/g, d.b.	18420	18815	19157	16743
C	%, d.b.	46.13	47.35	47.24	42.15
H	%, d.b.	5.99	6.06	6.19	5.51
N	%, d.b.	0.00	0.00	<0.05	0.23
O	%, d.b.	45.58	45.78	46.42	41.97
Al	mg/kg, d.b.	11.54	3.31	39.79	44.66
As	mg/kg, d.b.	2.09	0.20	BDL	BDL
B	mg/kg, d.b.	3.14	2.78	1.97	3.08
Ba	mg/kg, d.b.	14.04	4.66	10.23	4.50
Ca	mg/kg, d.b.	1795	2554	767	2935
Cd	mg/kg, d.b.	0.07	0.42	0.28	0.15
Co	mg/kg, d.b.	125.59	37.34	24.21	36.28
Cr	mg/kg, d.b.	0.27	0.13	0.17	0.69
Cu	mg/kg, d.b.	1.77	1.45	1.58	2.11
Fe	mg/kg, d.b.	15.55	22.01	35.05	44.14
K	mg/kg, d.b.	1214	1597	346	2055
Li	mg/kg, d.b.	0.03	0.07	0.02	0.01
Mg	mg/kg, d.b.	325	418	113	451
Mn	mg/kg, d.b.	42.35	7.12	157.88	8.94
Mo	mg/kg, d.b.	BDL	0.15	BDL	0.84
Na	mg/kg, d.b.	7.56	232.85	10.15	167.70
Ni	mg/kg, d.b.	1.22	0.48	0.53	0.60
P	mg/kg, d.b.	67.96	37.69	34.98	350.17
Pb	mg/kg, d.b.	0.16	0.15	2.92	0.23
S	mg/kg, d.b.	120.0	153.82	57.17	492.0
Sb	mg/kg, d.b.	0.87	0.24	BDL	0.46
Se	mg/kg, d.b.	BDL	BDL	BDL	0.21
Si	mg/kg, d.b.	65.45	27.66	95.60	26915
Sn	mg/kg, d.b.	0.89	0.76	0.30	0.22
Sr	mg/kg, d.b.	3.83	9.01	3.32	17.15
Ti	mg/kg, d.b.	0.98	3.92	2.93	2.07
V	mg/kg, d.b.	0.07	0.01	0.06	0.12
Zn	mg/kg, d.b.	3.07	21.76	14.54	8.11

d.b. = dry base, a.r. = as received, ND = not determined, BDL = below detection limit.
[a] Common beech (Fagus sylvatica).
[b] White poplar (Populus alba).
[c] European spruce (Picea abies).
[d] Winter wheat straw (Tatarus Sp.).

off-line as described above. For both the auger reactor as well as for the BFB reactor experiments, mass balances are estimated from the measured amounts of condensables (organics and (reaction) water), permanent gases and char. Not all condensable products can be analysed by the applied analytical procedures. This applies especially for the high-boiling fraction (e.g. ligin- and carbohydrate-derived oligomeric substances). It is estimated that the overall uncertainty in the calculated mass balance is approx. ±10 wt%.

3. Results and discussion

Table 3 contains the results of the chemical analysis of the chosen feedstocks. The main difference can be seen in the much higher ash content in the straw when compared to the woods. This translates especially into relatively high amounts of chlorine, sulphur, calcium, potassium and – most pronounced – silicon. The high amount of ash minerals in the straw will have an effect on its thermal degradation behaviour under pyrolysis conditions. Especially alkali metals are known to catalyse the thermal breakdown of carbohydrates [30,31].

Fig. 4 presents the TGA results for the selected feedstocks. At a first glance, the TGA curves for the four feedstocks look similar. Under the slow pyrolysis conditions of the TGA measurements, the bulk of the devolatilisation takes place in between 200 and 380 °C. At the final temperature of 500 °C, approx. 20–25 wt% of the original dry feedstock is left as char. All weight loss rate (differential thermogravimetry, DTG) curves clearly show three main regions. The small peak at low temperature (up to 100 °C) indicates the evaporation of residual moisture. Subsequently, the bulk of the devolatilisation takes place in two sequential steps, depicted by a more or less pronounced shoulder around 300 °C and a clear maximum around 350 °C. In agreement with previous work of Grønli et al. [27], the maximum mainly can be attributed to cellulose degradation, while the shoulder is representative for the decomposition of hemicellulose.

There is no well-defined hemicellulose degradation peak, because the temperature windows in which thermal degradation of hemicellulose and cellulose occurs, partially overlap. No clear features of the degradation of lignin can be seen, because of its wide range of thermal stability [32]. A closer look at the different DTG curves shows that the distinction between the shoulder and the main peak is clearest for beech, poplar and straw. For spruce, the shoulder is less pronounced and starts at a higher temperature. Also, the devolatilisation rate is somewhat smaller when compared to the other biomasses. The general idea is to identify suitable low degasification temperatures for hemicellulose and cellulose at which a high and selective conversion is possible without degrading too much of the lignin constituent. For the decomposition of the cellulose fraction this implies a temperature around the maximum in the DTG curve, while for the hemicellulose a temperature has been chosen, around the shoulder-temperature but below the estimated temperature of the onset of cellulose-decomposition. Results are presented in Table 4.

The overall results of the two-stage degasification experiments in the auger reactor are presented in Table 5 and Figs. 5 and 6. Fig. 5 presents the normalised results for the three main groups of pyrolysis products: permanent gases (CO, CO_2 and CH_4), condensables (water and organics) and char while the distribution of the organic condensables fraction is given in Fig. 6. This organic fraction of the condensables is subdivided into methanol, carboxylic acids, C_2–C_4 oxygenates, furans, levoglucosan, phenols and others (including unknown but GC-detectable components). From Fig. 5 it is obvious that the yields of gas, condensables and char do not differ very much for the different feedstocks. Gas yields

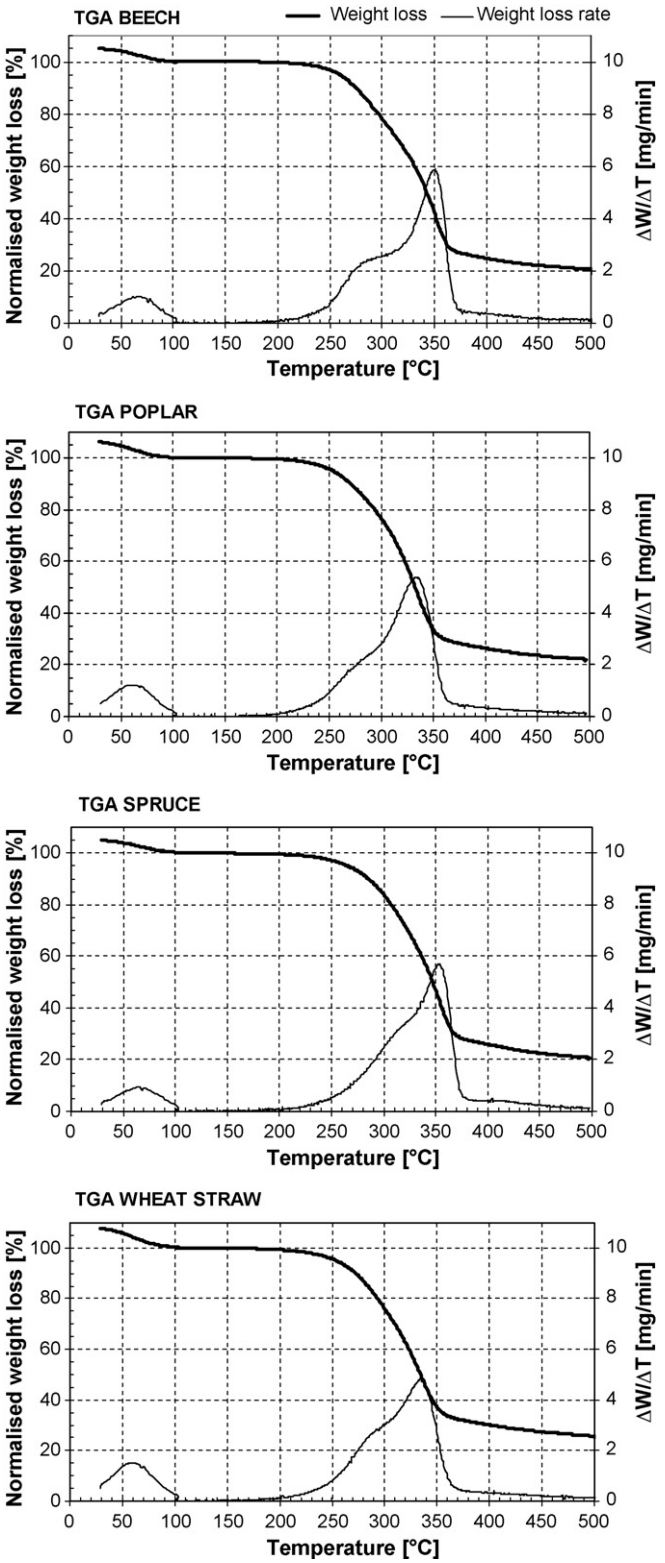

Fig. 4. TGA weight loss and weight loss rate curves for beech, poplar, spruce and straw.

range from 10 wt% (straw) to 15 wt% (beech), condensables are typically 40–50 wt% and the residual char amounts to approx. 40–50 wt%. For all feedstocks, the yield of CO_2 is approximately twice the yield of CO. Only minor amounts of methane are formed. The amount of organic condensables seems to be largest for the hardwoods beech and poplar (approx. 30 wt%) and smallest for

Table 4
From DTG selected temperatures (printed in bold) for two-stage degasification

Feedstock	Hemicellulose degradation			Cellulose degradation		
	T_{onset} (°C)	$T_{shoulder}$ (°C)	$\mathbf{T_{stage1}}$ **(°C)**	T_{onset} (°C)	T_{max} (°C)	$\mathbf{T_{stage2}}$ **(°C)**
Beech	240	300	**280**	310	350	**350**
Poplar	230	290	**280**	285	335	**350**
Spruce	253	320	**290**	300	355	**345**
Straw	240	295	**260**	270	335	**310**

straw (approx. 17 wt%). The amount of (reaction) water is largest for straw (24 wt%) and smallest for beech (12 wt%). Somewhat speculative, these results might indicate the effect of the inorganic constituents in the biomass, that are most abundant in the straw and catalyse cracking reactions, leading to water and char.

Table 5 shows that the yield of the organic condensable fraction is in all cases dominated by the amount of "others", predominantly unknown components. These constitute 55–60% of the total organic fraction. Carboxylic acids (mainly acetic acid) are the most abundant species in the remaining 40–45% of identified components. They constitute 12–15% of the total organic faction (2–3 wt% of the dry feedstock weight). The overall yields of phenols and methanol are highest for beech and poplar. This may be ascribed to the lesser thermal stability of the deciduous lignin when compared to the coniferous and herbaceous lignin of the spruce and – possibly – straw. It also indicates that both the phenolic compounds and methanol have lignin as their common origin. In general, the lignin in deciduous woods contains a mixture of predominantly guaiacyl and syringyl units, while the lignin from coniferous woods is almost exclusively built up from guaiacyl units. This originates from the biogenesis of lignin from the aromatic alcohols coumaryl alcohol, coniferyl alcohol and sinapyl alcohol as the main building blocks, yielding *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units in the final lignin structure. For beech (Fagus sylvatica) lignin, the relative content of these three units has been determined as G:S:H = 56:40:4 [33]. For spruce (Picea abies) lignin a ratio of G:S:H = 94:1:5 has been reported [34]. The differences in lignin composition with respect to the basic building blocks are illustrated by the guaiacol/syringol (G/S) ratio for the feedstocks which is approx. 0.5 for beech and poplar, 10 for spruce and 1 for straw. The total amounts of C_2–C_4 oxygenated

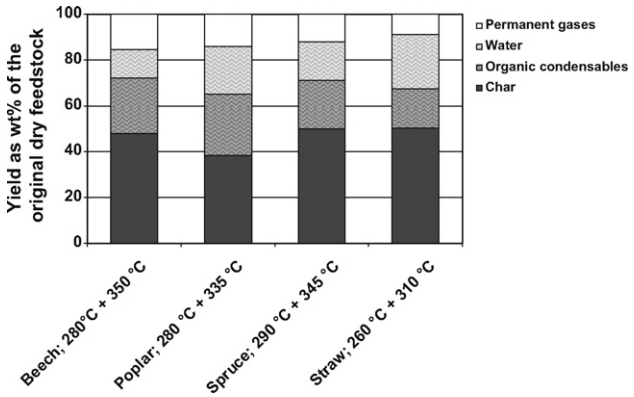

Fig. 5. Total normalised cumulative yields of gas, condensables and char from staged degasification of beech, poplar, spruce and wheat straw in the auger reactor.

degradation products are generally 1–2 wt% of the dry feedstock with acetol (hydroxy-propanone) and 1-hydroxy-2-butanone as main products.

Yields of the predominantly hemicellulose-derived furans are generally 1 wt% with furfural and furfuryl alcohol as main constituents. The amount of the cellulose-derived levoglucosan does not exceed 0.5 wt% of the dry feedstock. Summarising, except for carboxylic acids, the combined yields of potentially valuable chemicals and/or groups of chemicals from a two-stage low-temperature degasification process in the auger reactor are below 3 wt% of the dry feedstock. As can be seen from Table 3 and Fig. 6, for beech, this result is comparable or a little lower than the results from a one-step pyrolysis at the highest temperature (i.e. the temperature of stage 2). From Fig. 6 it can be seen that the two-staged approach leads to a somewhat better selectivity for acetic acid, that is relatively abundant in the product slate from the first stage. The results of the one-step degasification of beech wood at 350 °C are corroborated by recent work of Branca et al. who conducted a conventional fixed-bed pyrolysis with beech wood [35]. This agreement illustrates the fact that the auger facility can be regarded as a slowly moving, fixed-bed pyrolysis reactor.

Work of Roy et al. [8] provides an early example of a staged pyrolysis approach, using a multiple-hearth vacuum pyrolysis reactor. Using air-dry wood as feedstock, six pyrolysis-oil fractions

Table 5
Staged degasification results in wt% of the dry input of original feedstock in conventional pyrolysis experiments in the auger reactor

Pyrolysis products	Beech				Poplar			Spruce			Straw		
	Stage 1 280 °C	Stage 2 350 °C	Stage 1 + 2	Direct 350 °C	Stage 1 280 °C	Stage 2 335 °C	Stage 1 + 2	Stage 1 290 °C	Stage 2 345 °C	Stage 1 + 2	Stage 1 260 °C	Stage 2 310 °C	Stage 1 + 2
Total yield permanent gases	5.7	9.5	15.2	11.9	4.8	6.4	11.2	3.2	5.5	8.7	1.8	5.7	7.5
CO	1.4	3.2	4.6	3.6	1.4	2.4	3.8	0.8	2.4	3.2	0.6	1.9	2.5
CO_2	4.3	6.0	10.3	8.0	3.4	3.8	7.2	2.4	2.9	5.3	1.2	3.8	5.0
CH_4	0.02	0.6	0.6	0.3	0.02	0.1	0.1	0.02	0.2	0.2	0.0	0.03	0.03
Total yield condensables	4.8	31.6	36.4	40.3	16.6	21.3	37.9	11.2	16.3	27.5	18.1	16.1	34.1
Water	2.0	10.3	12.3	12.7	9.1	7.5	16.6	5.6	6.7	12.3	11.4	8.4	19.8
Total yield organic condensables	2.8	21.3	24.1	27.6	7.5	13.8	21.3	5.6	9.6	15.2	6.7	7.7	14.3
Methanol	0.1	1.7	1.8	1.4	0.3	0.8	1.2	0.3	0.3	0.7	0.3	0.5	0.8
Carboxylic acids	1.1	1.8	3.0	5.5	2.1	1.1	3.3	1.3	1.1	2.4	1.4	0.8	2.1
C_2–C_4 oxygenates	0.1	1.7	1.8	2.0	0.4	0.7	1.1	0.5	1.1	1.5	0.6	0.5	1.1
Furans	0.1	0.8	0.9	1.1	0.4	0.7	1.1	0.4	0.7	1.1	0.2	0.3	0.5
Levoglucosan	0.0	0.4	0.4	0.4	0.0	0.2	0.2	0.0	0.3	0.3	0.0	0.0	0.1
Phenols	0.1	2.0	2.1	1.7	1.1	1.6	2.6	0.2	0.6	0.7	0.2	0.6	0.9
Others (including unknowns)	1.2	13.0	14.2	15.5	3.1	8.7	11.9	2.9	5.7	8.5	4.0	5.0	8.9
Char	70.7	47.5	47.5	36.3	68.4	30.6	30.6	86.6	36.2	36.2	76.5	42.2	42.2
Mass balance	81	126*	99	89	90	85*	80	101	67*	72	96	84*	84

* Based on the yields (not shown) related to the input of the degasified material from stage 1.

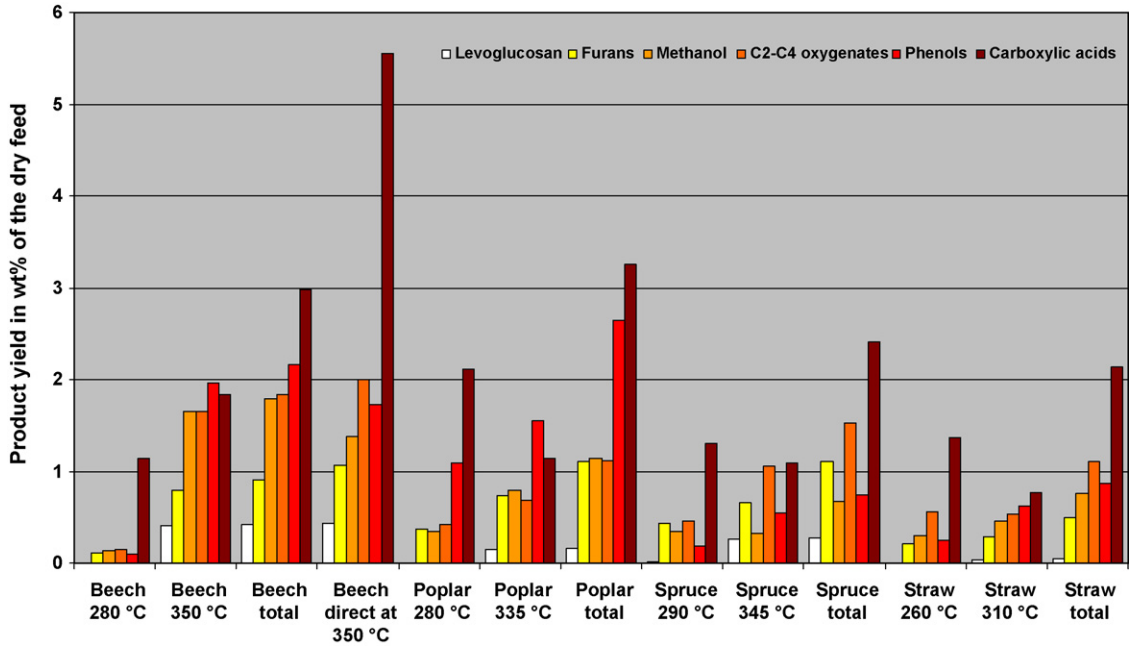

Fig. 6. Trend overview of yields of the major known condensable organics from staged degasification of beech, poplar, spruce and wheat straw in the auger reactor. Detailed data can be found in Table 5.

Table 6
Staged degasification results in wt% of the dry input of fresh feedstock

Pyrolysis products	Stage 1 200 °C	Stage 2 280 °C	Stage 3 350 °C	Stage 1 + 2 + 3	Direct 350 °C
Total yield permanent gases	0	4.8	7.4	12.2	12.1
CO	0	0.7	2.5	3.2	3.4
CO_2	0	4.0	4.8	8.8	8.5
CH_4	0	0.1	0.1	0.2	0.2
Total yield condensables	0.4	21.9	27.3	49.6	53.3
Water	0	13.1	11.5	24.6	26.8
Total yield organic condensables	0.4	8.8	15.8	25.0	26.5
Methanol	0.07	0.5	0.6	1.2	1.2
Carboxylic acids	0.2	3.7	1.9	5.8	6.3
C_2–C_4 oxygenates	0.0	0.5	1.6	2.0	2.3
Furans	0.05	0.4	1.0	1.5	1.6
Levoglucosan	0.00	0.04	1.0	1.0	1.4
Phenols	0.01	0.3	0.7	0.9	1.1
Others (including unknowns)	0.06	3.4	9.1	12.6	12.7
Char	ND	ND	ND	30.6	29.1
Mass balance	ND	ND	ND	92.4	94.5

were collected at reactor hearth temperatures of 200, 263, 327, 363, 401 and 448 °C, respectively. Although yields and selectivities of chemicals are limited, the approach clearly shows the potential of temperature-staging to obtain pyrolysis-oils that are concentrated with certain chemicals.

Table 6 presents the results of the three-staged degasification experiment and the direct pyrolysis with beech in the bubbling fluidised bed reactor.

The staged degasification experiment was conducted in the fluidised bed reactor without intermediate change-out of the bed and the char. So only the overall mass balance of the three stages could be estimated after completing the experiment. The results for the staged approach are almost identical to the results for the one-step pyrolysis and amount to 12 wt% permanent gases (CO_2:CO = 2.5:1), 50% liquid (half of which is water) and 30 wt% char. Approximately half of the fraction organic condensables is of unknown origin (12.6 wt% of the dry feedstock). Half of the fraction of identified organics consists of the carboxylic acids, mainly acetic

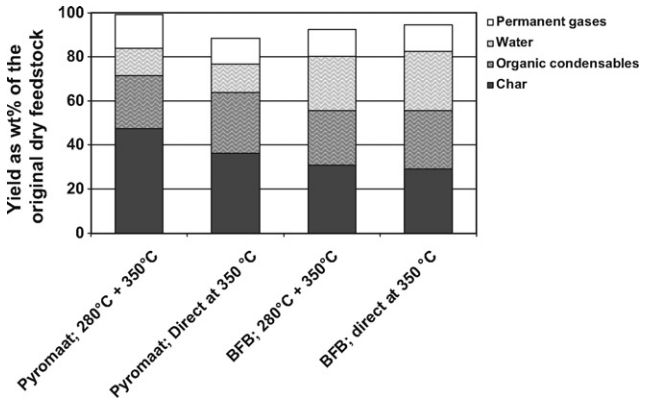

Fig. 7. Comparison of the overall yields of main products for the staged degasification of beech in the auger reactor versus staged degasification using bubbling fluidised bed reactor technology.

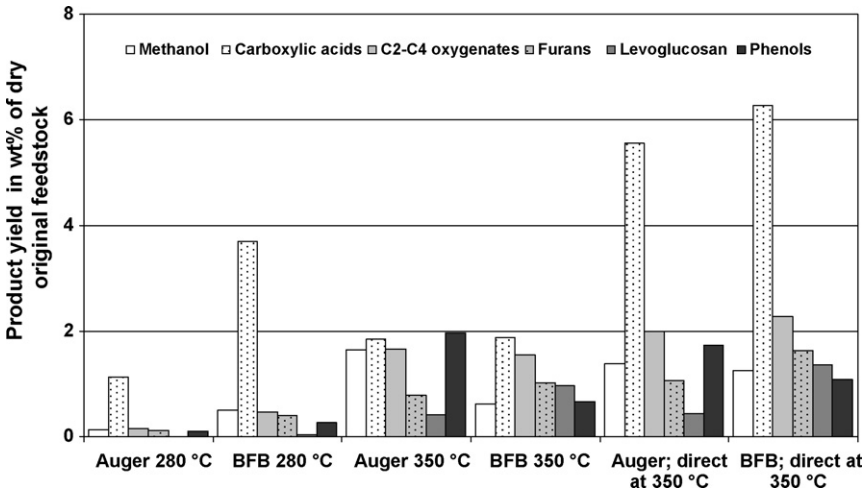

Fig. 8. Comparison of the yields of organic condensables per stage for the staged degasification of beech in the auger reactor versus staged degasification using a bubbling fluidised bed reactor.

acid. The yields of the other organic product groups amount to 1–2 wt% of the dry feedstock. Main individual species are methanol (1.2 wt%), acetol (1.5 wt%) and levoglucosan (1 wt%). Comparing the product yields from the separate stages, it can be seen that there is an overall increasing trend with increasing temperature. The exemptions are the yields of water and acetic acid that are highest at 280 °C. At 200 °C hardly any organics are liberated. The devolatilisation of the cellulose-derived anhydrosugar levoglucosan only starts at 350 °C. Roughly one third of the total yield of organic condensables originates at 280 °C. The bulk of the organic products (two thirds) is formed during stage 3 at 350 °C.

The results of the BFB experiments with beech seem similar to the results of the auger experiments. However, when looking into more detail, differences show up. Overall, the total amount of permanent gases is lower for the BFB approach (12 wt%) when compared to the auger reactor (15 wt%). Degasification of beech in the fluidised bed yields approx. 50 wt% of liquid against 40 wt% for the auger. Most of the auger reactor liquid is formed at 350 °C, while degasification in the BFB produces significant amounts of liquid at both 280 and 350 °C. Another large difference is the amount of char. Almost 50 and 40 wt% remain after respectively the two-staged and direct degasification in the auger reactor against 30 wt% for the staged and direct degasification in the fluidised bed. Results are presented in Fig. 7. In Fig. 8 the yields of the organic condensables are compared for both reactor approaches. It is clear that degasification of beech in the bubbling fluidised bed at 280 °C leads to higher yields of all products when compared to degasification in the auger. At 350 °C the yield of levoglucosan from the BFB degasification is more than twice the yield from the auger while the amounts of methanol and phenols are approximately three times lower. Apparently, the slow pyrolysis in the auger leads to an enhanced degradation of lignin at 350 °C, probably due to a longer residence time at high temperature and higher peak temperatures (up to 380 °C) in the reactor. Although the combined yields of potentially valuable chemicals and/or groups of chemicals from a two-stage low-temperature degasification process in a fluidised bed are in some cases higher than the corresponding yields from the auger approach, they are below 3 wt% of the dry feedstock (except for carboxylic acids). When compared to a one-step pyrolysis, the staged approach in the BFB offers a better selectivity for carboxylic acids at 280 °C, as was also the case for the auger reactor.

4. Concluding remarks

This paper describes experimental 'proof of principle' activities for staged degasification, a simple and elegant thermochemical conversion option to valorise lignocellulosic biomass. Due to the overlapping thermal stabilities of the main biomass constituents, degasification of the feedstock during a discontinuous step-wise temperature ramp in an auger reactor (a single screw moving-bed type of reactor), leads to complex mixtures of degradation products, with each staged degasification mixture consisting of small amounts of degradation products that originate from all three main biomass constituents. Except for acetic acid, yields of individual chemicals are generally below 1 wt% (based on the dry feedstock weight). However, certain groups of thermal degradation products like C_2–C_4 oxygenates and phenols are formed in higher yields up to 3 wt%. These results are roughly similar for the four selected biomass types beech, poplar, spruce and wheat straw. The only major difference is the higher yield of methanol and phenols for the deciduous beech and poplar woods when compared to the spruce and the straw. Slow pyrolysis of beech in a bubbling fluidised bed typically yields more water, less permanent gases and char, less methanol and phenols and more levoglucosan when compared to conventional pyrolysis in the screw reactor. The main reasons for these differences are the longer solid residence time and the large temperature gradients in the screw reactor when compared to the fluidised bed. Depending on the added-value of the product, a limited yield is not necessarily a drawback for a cost-effective process, provided that product selectivity is sufficient for effective separation and upgrading. Concluding, staged degasification is an elegant thermochemical conversion option to valorise lignocellulosic biomass but to increase product yields and/or selectivities, more R&D efforts are needed, especially towards optimisation of reactor conditions, application of catalysts and/or specific biomass pretreatments. Indeed, results of a hybrid degasification approach, involving a specific hydrothermal pretreatment and subsequent solid state ^{13}C NMR characterisation of the solid products, have indicated that significantly higher yields of value-added condensables can be achieved. This will be addressed in a subsequent paper. Finally, tuning staged degasification with product separation/upgrading technology is crucial for an economic process.

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